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Chinese Patent

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Filling Elastomer Combination.

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[57] Abstract

This invention concerns a halogen-free, thermoplastic elastomer combination. The combination includes (A) one kind of fire-retardant, halogen-free inorganic filler; (B) at least two kinds of elastomers coming from ethylene-propylene copolymer and terpolymer, polyamide, polyester, polyisobutylene, polyurethane, acrylate polymer, natural rubber, polybutadiene, polyisoprene, or graft copolymer or block copolymer containing polymer chain segments of at least two kinds of the above elastomers. In the combination, the weight percentage % of (A) is at least 50% of the total weight of (A) and (B). The combination also contains a small amount of antioxidant, mold discharging agent, carbon black, and other additives.

¹ Numbers in the margin indicate pagination in the foreign text.

Claims

What is claimed is:

1. A halogen-free, thermoplastic elastomer combination, which includes:

(A) One kind of fire-retardant, halogen-free inorganic filler;

(B) At least two kinds of elastomers coming from ethylene-propylene copolymer and terpolymer, polyamide, polyester, polyisobutylene, polyurethane, acrylate polymer, natural rubber, polybutadiene, polyisoprene, or graft copolymer or block copolymer containing polymer chain segments of at least two kinds of the above elastomers, whereas the weight percentage % of (A) is at least 50% of the total weight of (A) and (B).

2. The combination in Claim 1, whereas the inorganic filler comes from hydrated magnesia, aluminum hydrate, hydrated calcium silicate, clay, talc, carbonate, hydrate, oxide, other silicate, nitrogen/phosphorus combination and their mixtures.

3. The combination in Claim 1 or 2, whereas the proportion of inorganic filler is 50~75% weight of the combination.

4. The combination described in any one of Claims 1~3, whereas

the combination also contains additives of less than 15% weight of the combination, in addition to components (A) and (B).

5. The combination described in any one of Claims 1~4, whereas the ratio of the two elastomers ranges from 95:5 to 50:50 (in weight).

6. The combination described in any one of Claims 1~5, whereas the combination contains sufficient amount of vulcanizer that transforms the combination into thermosetting object upon being made to final shape.

7. The combination described in any of Claims 1~5, whereas the combination contains an elastomer vulcanizer; whereas the quantity of the vulcanizer is 1~90% of the amount required for basically complete vulcanization.

8. The combination described in any of Claims 1~7, whereas the inorganic filler is hydrated magnesia and the two elastomers are acrylate elastomer and ethylene-propylene elastomer.

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9. The combination described in any of Claims 1~7, whereas the inorganic filler is aluminum hydrate ($\text{Al}(\text{OH})_3$) and the two elastomers are:

(i) Acrylate elastomer and polyester elastomer;

(ii) Ethylene-propylene elastomer and polyester elastomer;

(iii) Polyester elastomer and polyamide elastomer; or

(iv) Polyamide elastomer and ethylene-propylene elastomer.

10. The combination described in any one of the Claims 1~5 or Claims 7~8, whereas the elastomers are partially crosslinked.

11. A product made through molding or extruding the combination described in any of the Claims 1~10.

12. A method for preparing halogen-free, thermoplastic elastomer combination, whereas the method includes mixing the following components:

(A) One kind of fire-retardant, halogen-free inorganic filler;

(B) At least two kinds of elastomers coming from ethylene-propylene copolymer and terpolymer, polyamide, polyester, polyisobutylene, polyurethane, acrylate polymer, natural rubber, polybutadiene, polyisoprene, or graft copolymer or block copolymer containing polymer chain segments of at least two kinds of the above elastomers, whereas the weight percentage % of (A) is at least 50% of the total weight of (A) and (B).

13. The method in Claim 12, whereas the filler and the elastomers are mixed with certain amount of elastomer vulcanizer; whereas the said amount is 1~90% of the amount required for basically complete vulcanization.

14. The method in Claim 12, whereas the thermoplastic elastomer combination is at least partially crosslinked upon radiation by high energy microwave or ultraviolet rays.

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15. The method in Claim 12, whereas the filler and the elastomers are mixed with vulcanizer sufficient enough to transform the combination into thermosetting object so as to process the combination into final shape and vulcanize the combination into thermosetting product.

16. A thermosetting combination prepared in accordance with the method in Claim 14 or 15.

17. A wire or cable with fire-retardant casing, whereas the casing is a blanket made through extruding the mixture of the following components:

(A) One kind of fire-retardant, halogen-free inorganic filler;

(B) At least two kinds of elastomers coming from ethylene-propylene copolymer and terpolymer, polyamide, polyester, polyisobutylene, polyurethane, acrylate polymer, natural rubber, polybutadiene, polyisoprene, or graft copolymer or block copolymer containing polymer chain segments of at least two kinds of the above elastomers, whereas the weight percentage % of (A) is at least 50%

of the total weight of (A) and (B).

Instructions

Filling Elastomer Combination

This invention concerns a halogen-free filling elastomer combination. The combination is fire retardant and contains inorganic filler. The quantity of the filler is at least 50% of the total weight of the filler and the elastomer altogether.

"Elastomer" is a rubbery polymer that can be extended to at least 2 times of the original length. When the tensile force is released, the polymer can fast contract to almost the original length. In non-crosslinking state and at room temperature, the modulus of elasticity of the elastomer measured with ASTM D638-72 method is about 10000psi (68.95MPa) or lower, while the rate of elongation is usually greater than 200%.

"Thermoplastic" material is a simple linear polymer or branch polymer that can be repeatedly softened, flow when heated, and return to solid state when cooled down to room temperature. The modulus of elasticity of the polymer measured with ASTM D638-72 method is usually greater than 10000psi (68.95MPa). When the thermoplastic material is heated to soften state, it can be molded or extruded into a product

of any predefined shape.

"Thermosetting" rubber or vulcanized rubber is a crosslinked polymer that is immobile or softened.

"Filler" is used in a variety of additives such as organic or inorganic materials. These materials can lower the combination cost and offer additional features such as fire resistance or combustion resistance, thus reinforcing or enhancing the combination.

Thermoplastic elastomers (TPEs) are materials that have the performance of elastomers and can be processed like thermoplastic plastics. TPEs are usually prepared through special block polymerization, or graft polymerization, or co-mixing of the two polymers. In all circumstances, a thermoplastic elastomer contains at least two kinds of chain segments, one is thermoplastic segment and the other is elastomeric segment.

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Block polymerized TPE has been described in the U.S. Patent 3,792,127, in which the block polymerization reaction between styrene and butadiene is published. TPE is comprised of polystyrene blocks and polybutadiene blocks. Polystyrene itself is a thermoplastic plastic while polybutadiene itself is an elastomer. Similarly, TPEs can be prepared through the U.S. Patent 3,265,765 by Holden et al.

or the branch polymerization method described in the article "Butyl Grafted to Polyethylene Yields Thermoplastic Elastomer" by Hartman et al. (Rubber World, page 59~64, October 1970). The article published a thermoplastic elastomer prepared through the method of grafting elastomer chain segment polyvinyl isobutyl to thermoplastic material polyethylene.

The other examples of producing TPE by combining thermoplastics and elastomers are described in the U.S. Patent 4,130,535 and U.S. Patent 3,806,558 by Coran.

It is a well-known method of using small amount (less than about 40% of the total weight) of filler such as talc, mica, titanitic oxide, calcium carbonate, and aluminum hydrate to lower product cost and improve product rigidity. For example, the U.S. Patent 3,965,055 by Shichman et al. published a vulcanized rubber made of rubber-resin combination (in which the resin particles are dispersed in the rubber). If necessary, other modifying or blending components (such as carbon black, clay, hydrated silicon oxide etc.) can be added to the rubber and resin. However, the vulcanized rubber made of such combinations is not thermoplastic but thermosetting rubber by definition.

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The thermoplastic combination published in the U.S. Patent

4,327,199 by Coran et al. consists of acrylic copolymer containing neutralizing acid obtained through simultaneously mixing thermoplastic crystalline polyester. The properties of the combination can be improved by adding other components (such as carbon black, silicon oxide, titanium oxide, pigment, clay etc.). The filler quantity usually varies in the range of about 15~80 weight shares in every 10 weight shares of rubber. In this sense, the filler accounts for only a small fraction of the whole combination (13~44%).

Some fillers such as antimonous acid anhydride and chloride or bromide can be applied to add other features such as fire resistance. For example, the U.S. Patent 4,275,180 by Clarke published a crosslinkable or crosslinked combination consisting of elastomers and thermoplastic polymers. Both the elastomers and thermoplastic polymers are basically halogen-free substances. However, all the implementations in Clarke's patent contain either chloride or bromide. Therefore, the whole combination contains halogen compound that may generate hydrochloric acid gas or other toxic and harmful vapors under high temperature and/or flame. These vapors make the combination unsuitable for application in closed space such as high-rise buildings and military and aerospace vehicles. In addition, the combination in Clarke's patent contains merely small amount of filler, which is

normally not over 40% of the total weight.

The U.S. Patent 4,108,962 by Pedlow published a fire-retardant external insulation adhesive tape for covering polyolefin insulation materials. This insulation adhesive tape made of mainly resin can be halogen thermoplastic plastic.

This invention concerns a halogen-free, thermoplastic elastomer combination, which includes:

(A) One kind of fire-retardant, halogen-free inorganic filler and

(B) At least two kinds of elastomers coming from ethylene-propylene copolymer and terpolymer, polyamide, polyester, polyisobutylene, polyurethane, acrylate polymer, natural rubber, polybutadiene, polyisoprene, or graft copolymer or block copolymer containing polymer chain segments of at least two kinds of the above elastomers, whereas the weight percentage % of (A) is at least 50% of the total weight of (A) and (B).

The combination preferably contains small amount of antioxidant, mold discharging agent, carbon black, and other additives. The total amount of the above additives does not exceed 15% of the total weight of the combination.

The combination can be partially crosslinked by means of conventional method of dynamic vulcanization of thermoplastic elastomers. The combination can also be fully or completely crosslinked through known method after being mold-pressed or extruded into final shape.

In a preferred implementation of the present invention, the halogen-free thermoplastic elastomer combination contains at least two kinds of elastomers as minor components. The total amount of the elastomers is lower than 50% of the total weight of the combination. A fire-retardant, halogen-free inorganic filler serves as the major component of the combination. The combination also contains a curing agent. It is important to notice that the combination does not contain conventional thermoplastic polymers such as polypropylene or polystyrene. The combination offers the following characteristics:

1. Low content of smoke dust and harmful gas;
2. Fire resistance;
3. Manufacturability similar to thermoplastic plastics; and
4. Special mechanical properties.

The halogen-free inorganic filler serving as the main component of the combination includes hydrated magnesia, aluminum hydrate, hydrated calcium silicate, clay, talc, carbonate, hydrate, oxide,

other silicates, nitrogen-phosphorus-contained additive releasing harmless gas and/or small amount of smoke dust, and other appropriate fillers referred in the present invention and listed in Page 253~263 of "Rubber World Magazine Blue Book" (Lippincott and Peto, 1984).

In the combination, one or several kinds of fillers are applied to provide comprehensive properties needed for a variety of special applications.

When aluminum hydrate ($\text{Al}(\text{OH})_3$) and hydrated magnesia are as used as the filler, the thermoplastic elastomer combination of the present invention has high Limit Oxygen Index (LOI) and basically does not release smoke dust during combustion. The low smoke dust and fire resistance are very important in many applications such as low-smoke, fire-retardant insulation cables used in buildings and military vehicles.

Nitrogen/phosphorus additive such as Char-Guard 329 supplied by Great Lakes Chemical Corporation can generate protective swelled coke in condensed phase when it is placed in flame (Char-Guard is a registered trademark). The coke provides excellent protection to the combination that is long and repeatedly exposed to fire, and basically solves the leaking problem commonly encountered. The low-content nitrogen/phosphorus additive not only provides excellent

protection, but also helps maintain excellent mechanical and electrical performances of the combination during the combustion test period.

Char-Guard 329 is stable in manufacturing conditions. It will not separate from the polymer and the specific weight of the polymer it composes is very low.

The preferred elastomers used in the present invention include elastic ethylene-propylene copolymer and terpolymer, polyamide elastomer, elastic polyester, isobutylene polymer, polyurethane polymer, acrylic acid elastomer, natural rubber, polybutadiene, polyisoprene, and other elastomers (sometimes called rubbers). These elastomers meet the following requirements:

1. In uncrosslinked state, the modulus of elasticity measured in accordance with ASTM D638-72 method at room temperature is 10000psi (68.94MPa) or lower;

2. The content of halogen is lower than 0.01% of the total weight;

3. The content of toxic gas such as hydrogen cyanide or carbon monoxide released during the heating process is not higher than 0.1% of the total weight.

Although it is recommended to use two or more elastomers to

obtain appropriate compound properties, block copolymer or graft copolymer elastomers constituted by two polymer elastomer chain segments can be employed in some cases to provide the needed operating characteristics. An example of such elastomer is polyester elastomer grafted with polybutadiene.

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The relative ratio of two elastomers changes in a wide range in order to obtain the needed mechanical properties and drawability. The tensile elongation is a qualitative measurement of thermoplastic property. The preferred ratio of each elastomer combination is determined by such technical conditions as "green strength", ratio of tensile modulus of elasticity, solubility parameter, and extent of vulcanization or crosslink of two elastomers.

The ratio of the selected two elastomers may change within the range from about 95:5 to 30:70 (weight ratio), while the preferred ratio may change within the range from about 95:5 to 50:50 (weight ratio).

In filling elastomer combination, the weight ratio of the filler (such as clay, mica, or aluminum hydrate) of the filler ranges from about 50% to 90%, while the best ratio is from about 50% to 70%. In some cases, it is probably beneficial to use two or more kinds

of fillers as some fillers help reduce smoke dust and offer other properties.

The vulcanization system used for partially or completely crosslinking the filling elastomer combination may include peroxide, sulfur, metal alkyl compound, epoxide, amine, azide, phenolic resin vulcanizer, metal oxide, quinone derivative etc.

The special type of vulcanizer to be applied is determined by the properties needed in specific vulcanized position in the polymer and finished product. A specific example is mentioned in the U.S. Patent 3,284,421 by Breslow and the U.S. Patent 3,297,674 by Breslow et al. Other proper vulcanizers are described in "Encyclopedia of Chemical Technology", Vol. 17 (published by Interscience, 1968, second edition); "Science and Technology of Rubber" (published by Academic Press, 1978, Chapter 7, Page 291~335, edited by F. R. Eirich); "Rubber Technology" (published by Van Nostrand Reinhold, 1973, second edition, Chapter 2, Page 19~50, edited by Maurice Morton); "Organic Peroxides" (Daniel Severn, Wiley Interscience, 1970) Vol. 1, and the U.S. Republished Patent 31,518 by Fischer from Column 3, Line 26 to Column 4, Line 35. These published documents are referred and integrated in the present invention.

The use level of elastomer vulcanizer is usually determined by the extent of thermoplasticity needed in the elastomer combination. To achieve partial vulcanization, the use level of vulcanizer is basically about 1~90%, preferably 5~75%, and best 10~40% of the use level necessary for complete vulcanization or crosslink. The accurate use level of elastomer vulcanizer is determined by manufacturers in consideration of such factors as the final method for elastomer production and the comprehensive properties needed in final use.

In the use of limited quantity vulcanizers or curing agents, it is necessary to well determine the mixing temperature of the combination containing vulcanizer, filler and elastomers. The vulcanizer of any use level should be basically consumed during the reaction.

It is generally considered that the vulcanizer in such a filler and elastomer combination is in proper use level, and that the combination has the desired resistance to deformation in high temperature and manufacturability like thermoplastic plastics.

Based on practical experience, the temperature of using at least 95% vulcanizer to decompose and generate free radicals within 0.5 minutes is used as the effective activation temperature of the vulcanizer. The vulcanizer with the activation temperature higher

than the softening point of the filling elastomer combination is preferred.

Vulcanizers with the activation temperature equal to or lower than the softening point of the filling elastomer combination can also be used. The activation temperature is usually higher than 240°F (116°C), and is preferably 300°F (149°C).

The highest activation temperature is usually not higher than 450°F (232°C), and is preferably not higher than 400°F (204°C). The specifications of common peroxide vulcanizers such as 2, 5-di-(*tert*-butylperoxy)-2, 5-dimethylethane (peroxide I) and dicumyl peroxide (peroxide II) are listed in the following table.

Temperature		Half-life in Methylbenzene	
°F	(°C)	Peroxide I	Peroxide II
240	(116)	21 hours	10.2 hours
270	(232)	2 hours	1.75 hours
335	(168)	5 minutes (calculated)	3 minutes (calculated)
360	(182)	47 seconds	22 seconds
390	(199)	7.2 seconds	3.6 seconds

As shown in the above table, at 360°F (182°C), the times needed for decomposing 95% of peroxide I and peroxide II is about 4 minutes and 1.5 minutes, respectively.

The efficacy of vulcanizer should be basically exhausted in the dynamic partial crosslinking treatment so that almost no further vulcanization will occur afterwards. When the dynamic partial vulcanization finishes, it is desirable to add small amount of free radical collecting agent (such as stabilizer or antioxidant) to the combination in order to further ensure to terminate the effect of any residual crosslinking vulcanizer.

Such stabilizer can be added and mixed in the last moment of mastication. The dynamic partial vulcanization material can be undertaken one or more times of "refining" in the mixing mill, while the stabilizer or antioxidant can be added during the refining process or just before refining begins.

Full vulcanization will change the combination properties and alter the combination to non-thermoplastic combination, i.e., thermosetting combination, which is an additional content of the present invention. In this case, the thermoplastic combination is mold pressed or extruded into final shape or pattern, and is activated by vulcanizer to transform into thermosetting object.

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Elastomer vulcanizer can be used exclusively or together with accessory ingredients such as accelerant, activating agent,

stabilizing agent, free radical collecting agent, chain extension agent, and antioxidant.

These accessory ingredients include 3-aldol- α -naphthylamine, 2, 2, 4-trimethyl-1, 2-dihydroquinoline, diphenylamine acetone condensation compound, octyl-diphenylamine, N-phenyl-N'-cyclohexyl-ursol, 2, 6-di-tert-butyl-4-methylphenol, styrene-resorcinol resin, metacresol monosulfide, di-paracresol-2-propane, 2, 5-di-tert-amylhydroquinone, dilauryl-3, 3'-sulfhydryl-dipropyl acid, and similar dialkyl sulfhydryl-dipropyl acid. Colorant such as carbon black can also be applied.

Other appropriate additives are listed in Page 244-256 in "Rubber: Natural and Synthetic", Stern, (Palmerton Publishing Company, New York, 1967), and "Chemistry and Technology of Rubber", Davis and Blake (Reinhold, New York, 1937).

The partial vulcanization of the filling elastomer combination is accomplished through exposing the combination to vulcanizer or crosslinking agent in which the use level is not enough to basically crosslink and vulcanize the combination.

Apart from ensuring that the use level of elastomer vulcanizer or crosslinking agent is less than the use level needed for complete

vulcanization or crosslinking, it is also necessary to carefully control some parameters such as vulcanization temperature and vulcanization time in order to ensure complete activation of the vulcanizer in the combination. In this aspect, a variety of vulcanizers can be applied. The variation of the vulcanization temperature of the filling elastomer combination ranges from about 160°F to 400°F (71°C to 204°C), preferably from 220°F to 400°F (104°C to 204°C), and best from 320°F to 400°F (160°C to 204°C). The vulcanization temperature is restricted by the stability of specific elastomers used in the combination. For example, the combination filled with acrylic ester elastomer and polyester elastomer cannot be processed at the temperature higher than about 400°F (204°C) or lower than about 320°F (160°C). When the temperature is higher than 400°F (204°C), the acrylic ester degrades and releases decomposing gas. When the temperature is lower than about 320°F (160°C), the polyester elastomer is close to the melting point and thus cannot be processed.

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The vulcanization time, which is generally determined by the vulcanization system and temperature applied, may range from 1 minute to 30 minutes, and preferably from 3 to 20 minutes. It goes without

saying that the time needed for dynamic partial vulcanization also varies depending on some parameters such as specific polymers used in the combination, vulcanizer type and user level, as well as temperature for partial vulcanization.

For the purpose of obtaining the optimum dynamic partial vulcanization result, the fillers, elastomers, and vulcanization system can be exposed in a mixing mill or closed blender such as Banbury blender, or extrusion-blender, or transfer blender.

One easy combining method is to pre-mix each component, and then use preheated extruder to extrude the co-mixed combination. Other mixing installations such as Brabender blender, Banbury blender, and roll blender can be employed for this process. Since vulcanizers undertake crosslinking reaction to some extent at high temperature, it is unnecessary to conduct such reaction in a closed container. A conventional single-worm or multi-worm extruder is the most ideal reaction container as it can accomplish combining work without the need of auxiliary apparatus. Other appropriate installations include Gelmat blender, blending-extruding machine, and continuous and intermittent blender.

If necessary, a small amount of monomers can be added randomly to enhance the degree of vulcanization through forming some graft

or co-graft polymers. The combined product can be retrieved by means of any methods or equipment in any circumstances. These methods or equipment can separate or make use of this "filling elastomer combination". The retrieved combination may be in the form of deposited fine hair objects, particles, and powders, or further combined particles or powders, or formed product made from the filling elastomer combination.

The manufacturability of filling elastomer combination can be evaluated through sample test based on different applications. The sample is tested on the surface manufacturing smoothness and is qualified if there is basically no glaring defects on the surface.

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Non-thermoplastic material surface is rough, uneven, and unclear in outline. Although these standards are qualitative, those skillful in the art can easily identify qualified product from the unqualified ones through apparent test and contact.

The manufacturability of the combination provided in the present invention can be evaluated through forming operation such as extrusion, injection, or die pressing of the combination sample.

The extrusion forming method is applied to test production-purpose uninterrupted products such as hose, window

sealers, wire coating, and flat board. It is important to examine the surface smoothness of the extruded product. The extrudability is evaluated according to ASTM D2230.

In order to achieve satisfactory injection forming result, the filling elastomer combination must form uniform intensity in the mold. The flow viscosity property of the elastomer combination should ensure to correctly inject the combination into the mold under operating conditions.

The elasticity of the formed product made from the thermoplastic combination provided in the present invention can be tested through low-elongation permanent deformation based on ASTM D-412.

The thermoplasticity of the combination provided in the present invention can be tested by means of the repeated manufacturability of the combination, especially the ability to keep the needed properties when the combination is re-extruded.

In the processing the combination provided in the present invention, the addition of mold discharging agent or lubricant can be beneficial, especially from the viewpoint of improving the extrusion quality of the combination. Any known lubricants commonly applied in rubber or plastics processing can be used for this purpose.

In the filling elastomer combination, the use level of lubricant is about 0.2~3 shares of weight in every 100 shares of weight of elastomer, and is preferably about 0.5~1 share of weight.

In addition, it is preferable to contain stabilizers in all combinations. The use level of the stabilizer can be about 0.5~5 shares of weight of thermoplastic combination, and is preferably 0.5~5 shares of weight. In the stabilizer system, the type and use level of each stabilizer are determined by the final use of specific elastomers and filling combinations.

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For example, a stabilizer system is used in a typical combination consisting of hydrated magnesia elastomer, acrylic acid elastomer, and ethylene-propylene elastomer. The stabilizer system contains 0.2% hindered phenol antioxidant (such as Cyanox 1790 made by American Cyanamid), 0.2% calcium stearate and 0.2% sulfite accessory antioxidant (such as Irgaphos 168 made by Ciba Geigy). If the final place of use also includes outdoor long-time exposure to the Sun, ultraviolet stabilizer such as 0.3% hindered amine (such as Hostavin N20 made by American Hoechst). The weight ratio of all the above stabilizers is based on the weight of elastomers.

In another typical combination consisting of hydrated alumina,

acrylate elastomer, and polyester elastomer, it is discovered that a stabilizer system comprising of three components is particularly suitable for obtaining the required product. In the stabilizer system, the first component contains a high molecular weight, multi-functional group space hindered phenol such as tetra- [methylene 3-(3', 5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane ("tetramethane" for short), which can be purchased from Ciba Geigy Inc. with the registered trademark of Irganox 1010. This high molecular weight, multi-functional group space hindered phenol plays a role as an antioxidant and thermal stabilizer.

The second component of the stabilizer system is alkyl ester of thiohydroxy acid such as dilaurate-thiohydroxy-dipropyl ("DLTDP"). This component serves as an accessory antioxidant.

The third component of the stabilizer system is substituted azimino-benzene. This component in the stabilizer helps the elastomer combination to resist ultraviolet radiation.

Naugard 455 made by Uniroyal Inc. can also be employed as part of the stabilizer system. The stabilizers are not limited to those mentioned above. In fact, any suitable stabilizer system known by those skillful in the field of polymer stabilization technology field can be employed.

The elastomer combination can be produced in accordance with one-step operation or multi-step operation method.

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In the one-step operation method, the filler, elastomer and vulcanizer are added in required ratio to a proper blender such as Banbury closed blender, transfer extrusion-blender, extruding machine, or any equipment that can effectively blend the combination at the required temperature. The blending installation can be pre-heated in order to reduce the time needed for reaching the processing temperature range.

The combination is kept at the processing temperature and blended continuously for a while to ensure that the combination effectively undertakes partial vulcanization.

During the operation, the stabilizer system is exposed to the combination and the operation is continued for a while, which is usually about 1 minute or longer so as to completely blend stabilizer into the combination and to deactivate any residual vulcanizer.

In the multi-step operation method, the selected elastomer and vulcanizer is added to appropriate equipment for partial vulcanization. After that, the partially vulcanized elastomer is combined with other selected elastomers, fillers, and needed

components.

As mentioned above, the polymer combination is halogen free, which reduces the possibility of releasing HCl, HB, or other toxic gases. Besides, the combination provided in the present invention may contain other additives such as stabilizer, antioxidant, free radical collecting agent, ultraviolet stabilizer, anti-hydrolysis stabilizer, acid acceptor, colorant, and pigment. The use level of the additives is preferably not over 15%, and best not over 10%.

Another method for crosslinking of the combination provided in the present invention is to apply high energy, microwave, or ultraviolet radiation. The range of radiation dosage needed for complete vulcanization is from 2 to 100 millirad or even higher, but is preferably from 4 to 60 millirad. As far as partial crosslinking is concerned, the dosage of 0.5-10 millirad is effective depending on specific elastomers in the combination.

In some cases, it might be necessary to add coagents in the crosslinkable polymer combination in order to promote crosslinking reaction. These coagents usually contain multiple unsaturated radicals such as alkenyl group or acrylate. Although the actuation mechanism is unknown, the coagents are considered to react with primary free radicals formed on the main chain of the polymer to

constitute even more stable free radicals, making the crosslinking through coupling reaction easier than that through chain cleavage reaction.

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Coagents may come from N, N'-metaphenylene-dimaleimide, trimethylol-propane-trimethyl-acrylate, tetraallyl oxy-ethane, triallyl cyanurate, triallyl isocyanurate, acrylic tetramethylene ester, or polyoxyethylene diol-dimethyl acrylate. The use level of coagent in every 100 shares of elastomer combination is preferably up to 5 shares (weight), and best 1~3 shares (weight).

The filling elastomer combination provided in the present invention can be used in many applications. The preferred combination can be applied in special situations such as hydrocarbon fluid resistance and thermal ageing resistance situations. Therefore, the combination can be used as wire and cable line material and conducting material, especially as panel and board in the interior of elevators, vessels, space vehicles, high rise buildings, and other closed spaces where dangerous toxic smoke may be generated when they are on fire.

The combination of the present invention has the following unique comprehensive characteristics:

1. When placed in flame, it only releases small amount of harmful

gas and almost no smoke dust;

2. It is fire-retardant;

3. It still offers manufacturability like thermoplastic plastics even the combination contains fillers and elastomers. The combination does not have to contain conventional thermoplastic plastics (such as polyethylene, polypropylene and polystyrene);

4. It has excellent mechanical properties, especially tensile and anti-tearing properties.

In the following non-restrictive implementations of the present invention, all percentages, unless otherwise indicated, are based 100% weight of elastomers and fillers. Other additives, such as vulcanizer, mold discharging agent, carbon black, stabilizer, antioxidant, are expressed based on the weight of the filling elastomer combination.

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The objective of the following implementations is to show the formulations of the combination, and demonstrate that the combination is thermoplastic and can be die-pressed or extruded into high quality insulation tape, decorative board, panel, wire and other products while reaching the minimum values of most (if not all) of the following properties:

Property	Test	Value
1. Tensile Intensity	ASTM D-412	>1000psi (6.89Mpa)
2. Elongation at Break	ASTM D-412	>130%
3. Anti-tearing	ASTM D-470	>30lbs/in (52N/cm)
4. Hardness (Shore A)	ASTM D-2240	>75A
5. Limit Oxygen Index	ASTM D-2863	>30%
6. Smoke Dust Test	ASTM D-2863	Almost no smoke dust
7. Smoke Dust Analysis	*	Low concentration of harmful gas
8. Halogen Content in General Formulation of Combination	Calculation	<0.1%
9. Moldability Using Die Pressing Method	Visual observation	Good surface quality
10. Extrudability Using Laboratory Extruder	Visual observation	Good extrudability
11. Smoke Generation Test-Average Dust Optical Density at Dust Generation	ASTM E662-83	<160

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* The No. 7 test (Smoke Dust Analysis) is conducted using Draeger comparison tubes. The concentration of all harmful gases (HCN, NO_x, SO₂, H₂S, HCl, HBr, HF and all hydrocarbon gases) should not exceed 100ppm in combustion state and 30ppm in non-combustion state. As for carbon monoxide, the standard maximum concentration is 1000ppm in combustion state and 300ppm in non-combustion state.

Implementation 1 (for comparison purpose)

Based on the U.S. Patent 4,275,180 by Clarke, the following compositions are used to prepare the combination according to the steps described in Column 7 of the Patent:

Composition	Weight in Share	Weight in %*
Ethylene Methyl Acrylate Elastomer	123	57.75
Carbon Black	21	--
Antimonous Acid Anhydride	15	7.04
Dechlorane Plus 25 (Chloride fire-retardant)	15	7.04
Octadecyl Amine (Mold discharging agent same as Crodamine IHT)	3	--
Triallyl cyanurate	4	--
Block Copolyester	60	28.17
Total	241	100.00

* The weight % does not include vulcanizer, carbon black, stabilizer, and mold discharging agent.

Once the preparation finishes, the combination is extruded and then irradiated at 12 millirad dosage. The mechanical property test and smoke analysis are conducted. The results are obtained as follows:

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Halogen Content: 5.16%

Tensile Strength: 1798psi (12.4MPa)

Elongation at Break: 500%

Anti-tearing Strength: 50.31 lb/in (88.1N/cm)

Hardness (Shore A): 72A

Limit Oxygen Index: 22%

Smoke Analysis	Gas	Combustion	Non-combustion
(ppm value)	HCN	26.0	14.8
	NOx	41.2	8.0
	SO ₂	25.0	1.3
	H ₂ S	0.8	0.2
	HCl	31.2	20.3
	HBr	--	--
	HF	6.0	0.1
Harmful Gas		130.0	44.7
	CO	1068.0	719.0
Smoke Generation Test:	Combustion		227
	Non-combustion		281
	Average		254

Since this formulation has low filler content (14%), high halogen content (5.16%), low limit oxygen index (22%), and high content of harmful gas generated during combustion, the formulation

in this implementation does not fall into the scope of the present invention.

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Implementation 2 (for comparison purpose)

Based on the formulation and steps provided in Implementation 3 of the U.S. Patent 4,275,180, the following combination is prepared using a laboratory Banbury closed blender:

Composition	Weight in Share	Weight in %*
Ethylene Methyl Acrylate Elastomer used in Implementation 1	30	31.9
Carbon Black	2	--
Antimonous Acid Anhydride	6	6.4
Decabromodiphenyl Oxide	12	12.8
Octadecyl Amine (Mold discharging agent same as Crodamine IHT)	0.375	--
Triallyl cyanurate	1	--
Irganox 100	0.375	--
Calcium carbonate	16	17.0
Hytrel Thermoplastic Elastomer Used in Implementation 3 of the Above-mentioned Patent	30	31.9
Stabilizer	2.25	

* The weight % does not include vulcanizer, carbon black, stabilizer,

and mold discharging agent.

The combination is blended in a rubber mixing mill, made into panel through press forming method, and then irradiated at 12 millirad dosage. The results are obtained as follows:

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Halogen Content:	10.25%
Tensile Strength:	1658psi (11.4MPa)
Elongation at Break:	5.75%
Anti-tearing Strength:	52.0 lb/in (91.1N/cm)
Hardness (Shore A):	84A
Limit Oxygen Index:	21%

Smoke Analysis	Gas	Combustion	Non-combustion
(ppm value)	HCN	8.5	12.0
	NOx	35	8.0
	SO ₂	0.0	0.0
	H ₂ S	0.6	0.0
	Hydrocarbon	95.0	125.0
	HCl	2.5	5.7
	HBr	88.5	35.0
	HF	1.7	0.2

Harmful Gas Total	130.0	185.9
CO	1068.0	444.0
Smoke Generation Test:	Combustion	147
	Non-combustion	167
	Average	157

Since this formulation has low filler content (36.2%), high halogen content (10.25%), low limit oxygen index (21%), and high content of harmful gas generated during combustion, the formulation in this implementation does not fall into the scope of the present invention.

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Implementation 3

The following compositions (all weights are counted in percentage and do not include stabilizer, mold discharging agent, carbon black or vulcanizer) are used to prepare filling elastomer combination.

Composition	Weight %
(a) Aluminum hydrate (ATH) with 0.8mm average particle diameter and 4m ² /g BET surface area	52.9
(b) Ethylene Methyl Acrylate Elastomer	

containing 20% silicon dioxide and having 6.40% 33.5

elongation and 30ML(H-4) Mooney viscosity

(212°F)

(c) Block Copolyester Elastomer having 1.18

specific weight, 40D hardness, and 170% 13.6

elongation

The above compositions are blended in a laboratory Banbury blender to prepare the combination. The combination also contains 2.63% weight carbon black, 0.58% weight vinylsilane, 0.39% weight stabilizer system, and 1.74% weight triacryl cyanurate. The stabilizer system is composed of 1 share of Irganox 1010, 1 share of Tinuvin 327, and 4 shares of DLTDF. The combination is pressed to become narrow strips, extruded into tapes, and then irradiated at 15 millirad dosage. The results are obtained as follows:

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Test

Tensile Strength:	1904psi (13.13MPa)
Elongation at Break:	200%
Anti-tearing Strength:	47 lb/in (82.3N/cm)
Hardness (Shore A):	89A

Limit Oxygen Index: 34%

Smoke Dust Test: Very little smoke

Halogen Content: 0.0067%

Smoke Generation Test: Combustion 37; Non-combustion 154; Average
95.5

Smoke Analysis	Gas	Combustion	Non-combustion
(ppm value)			
	HCN	6.2	4.0
	NOx	37.0	0.0
	SO ₂	0.0	0.0
	H ₂ S	0.7	0.0
	Hydrocarbon	46.0	11.7
	HCl	2.7	3.3
	HBr	0.0	0.0
	HF	0.1	0.1
	Harmful Gas Total	92.7	19.1
	CO	875.0	269.0

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Implementation 4

The filling elastomer combination containing the following compositions is prepared in a large Banbury blender (all weight % does not include carbon black, vulcanizer, stabilizer or mold

discharging agent):

Composition	Weight%
(a) Aluminum hydrate (ATH) identical to that in Implementation 3	53.8%
(b) Polyester elastomer identical to that in Implementation 3	15.4%
(c) Ethylene-propylene acrylate rubber identical to that in Implementation 3	30.8
Total	100.0

The combination also contains 7.24% carbon black, 0.27% vinylsilane as mold discharging agent, 0.47% stabilizer system used in Implementation 3, and 0.15% VAROX peroxide as vulcanizer produced by R. T. Vanderbilt.

The combination is pressed to become narrow strips, extruded into tapes, and then tested. The results are obtained as follows:

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Test

Extrudability:	Excellent
Tensile Strength:	935psi (6.4MPa)
Elongation at Break:	310%

Anti-tearing Strength: 53 lb/in (92.8N/cm)

Hardness (Shore A): 78A

Limit Oxygen Index: 32%

Smoke Dust Test: No smoke

Halogen Content: 0.00786%

Moldability: Excellent

Smoke Generation Test: Combustion 153; Non-combustion 152;

Average 152.5

Smoke	Gas	Combustion	Non-combustion
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Analysis

(ppm value)	HCN	1.0	1.2
	NOx	0.1	0.0
	SO ₂	0.0	0.0
	H ₂ S	0.7	3.3
	Hydrocarbon	245.0	18.3
	HCl	3.8	2.5
	HBr	0.0	0.0
	HF	0.2	0.1
Harmful Gas Total		256.8	25.4
	CO	767.0	208.0

Implementations 5 and 6

Two combinations are prepared by following the same steps as Implementation 4 and using slightly different ratios as follows. The sum of weight percentages of (a), (b) and (c) is 100%. Other additives are also counted in weight percentage of the total weight.

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Implementation 5

Composition	Weight%
(a) ATH identical to that in Implementation 3	50.26
(b) Polyester elastomer identical to that in Implementation 3	14.37
(c) Ethylene-propylene acrylate rubber identical to that in Implementation 3	35.37
Total	100.00%

The combination also contains 2.59% carbon black, 0.57% stabilizer system used in the above implementation, and 0.29% VAROX peroxide vulcanizer.

The combination is blended and tested. The results are obtained as follows:

Tensile Strength:	893psi (6.16MPa)
Elongation at Break:	290%

Anti-tearing Strength:	41.1 lb/in (72N/cm)
Extrudability:	Excellent
Limit Oxygen Index:	35%
Smoke Dust Test:	No smoke
Halogen Content:	0.00752%

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Implementation 6

Composition	Weight%
(a) ATH identical to that in Implementation 3	53.63
(b) Polyester elastomer identical to that in Implementation 3	13.38
(c) Ethylene-propylene acrylate rubber identical to that in Implementation 3	32.99
Total	100.00%

The combination also contains 2.59% carbon black, 0.57% vinylsilane mold discharging agent, 0.40% stabilizer system used in Implementation 3, and 0.26% VAROX peroxide vulcanizer.

The combination is blended and tested. The results are obtained as follows:

Tensile Strength:	1062psi (7.32MPa)
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Elongation at Break:	270%
Anti-tearing Strength:	28.8 lb/in (50.4N/cm)
Extrudability:	Excellent
Limit Oxygen Index:	--
Smoke Dust Test:	No smoke
Halogen Content:	0.00697%

Implementation 7

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A combination is prepared by following the same steps as Implementation 4 and using polyester elastomer with 40D hardness, 1.16 specific weight, and 560% elongation. The weight percentages are identical to that described in Implementation 5. The properties of the thermoplastic combination made from the filling elastomer are as follows:

Tensile Strength:	622psi (4.29MPa)
Elongation:	335%
Anti-tearing Strength:	42.6 lb/in (74.6N/cm)
Extrudability:	Excellent
Smoke Dust Test:	No smoke
Halogen Content:	0.00752%

Implementation 8

A combination is prepared by following the same steps as Implementation 6, except that ATH in Implementation 6 is replaced by magnesia. The extrusion of the combination is somehow difficult. The properties of the combination are as follows:

Halogen Content:	0.00697%
Tensile Strength:	2055psi (14.17MPa)
Elongation:	120%
Anti-tearing Strength:	35.5 lb/in (62.17N/cm)
Limit Oxygen Index:	31%
Shore's Hardness:	93A
Smoke Dust Test:	No smoke, low toxicity

Implementation 9

A combination is prepared by following the same steps as Implementation 6, except that ethylene-propylene acrylate rubber is replaced by ethylene-propylene-hexadiene terpolymer. This thermoplastic combination has the following properties:

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Thermoplastic extrudability:	Excellent
Tensile Strength:	1091psi (7.52MPa)
Elongation:	130%

Shore's Hardness:	90A
Anti-tearing Strength:	31 lb/in (54.29N/cm)
Smoke Dust Test:	No smoke, low toxicity
Halogen Content:	0.00697%

Implementation 10

A combination containing the following compositions is prepared in a laboratory Banbury blender.

Composition	Weight%
Ethylene-propylene acrylate rubber used in Implementation 3	30.8
Polyester elastomer used in Implementation 3	15.4
ATH used in Implementation 3	51.6
Talc	2.2
Total	100.00%

The combination also contains 7.6% carbon black, 0.27% vinylsilane mold discharging agent, 0.15% Varox vulcanizer, and 0.46% stabilizer system used in Implementation 4.

In the test, the prepared filling elastomer combination is extruded like thermoplastic plastic. The combination has the following properties:

Halogen Content:	0.0076%
Tensile Strength:	1167psi (8.05MPa)
Anti-tearing Strength:	45 lb/in (78.81N/cm)
Elongation at Break:	165%
Shore's Hardness:	79A
Limit Oxygen Index:	31%
Smoke Dust Test:	No smoke
Extrudability:	Excellent

Implementation 11

Except that the polyester elastomer in Implementation 4 is replaced by another polyester with 60D Shore's hardness, 6100psi tensile strength, 400% elongation at break, and 1.24 specific weight, a combination similar to that of Implementation 4 is prepared. The following results are obtained:

Halogen Content:	0.00786%
Tensile Strength:	1129psi (7.78MPa)
Elongation at Break:	190%
Anti-tearing Strength:	36 lb/in (63N/cm)
Shore's Hardness:	80A
Limit Oxygen Index:	32%

Smoke Dust Test: No smoke

Extrudability: Excellent

Implementation 12

The combination similar to that of Implementation 4 is prepared by adding materials in two times in a laboratory Banbury blender. The ATH used in Implementation 4 is replaced by the ATH with $0.5\mu\text{m}$ average diameter, $7\text{m}^2/\text{g}$ BET surface area treated with propylene acrylate rubber. Besides, the polyester elastomer is grinded into 20-mesh powder before it is added into Banbury blender. The filling elastomer combination has the following properties:

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Halogen Content: 0.00786%

Tensile Strength: 1543psi (10.64MPa)

Elongation at Break: 205%

Anti-tearing Strength: 31 lb/in (54.29N/cm)

Shore's Hardness: 84A

Limit Oxygen Index: 32%

Smoke Dust Test: No smoke

Extrudability: Excellent

Implementation 13

The combination similar to that of Implementation 4 is prepared.

In the preparation, the propylene acrylate rubber used in Implementation 4 is replaced by ethylene-methyl acrylate co-polymer with 1.12 specific weight, 1300% elongation at break, and 29ML(1+4) Mooney's viscosity at 212°F. The test results show that the combination has the following properties:

Tensile Strength:	1012psi (6.98MPa)
Extrudability:	Excellent
Elongation:	170%
Halogen Content:	0.00786%
Shore's Hardness:	84A
Anti-tearing Strength:	31 lb/in (54.29N/cm)
Smoke Dust Test:	No smoke
Limit Oxygen Index:	33%

Implementation 14

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The combination containing the following compositions is prepared by following the steps in Implementation 3:

Composition	Weight%
ATH used in Implementation 12	52.5%
Polyester elastomer used in Implementation 3	15.8%

Propylene acrylate elastomer used in 31.7%

Implementation 3

Total 100.00%

The combination also contains 7.44% carbon black, 0.28% vinylsilane mold discharging agent, 0.31% stearic acid processing agent, 0.15% Kemamine 990D mold discharging agent produced by Humko Products, 2.22% Nauguard 455 antioxidant produced by Uniroyal, 0.555% DLTD oxidant promoter, and 0.155% VAROX powder vulcanizer produced by R. T. Vanderbilt. All percentages are based on 100% of the weight of the above-listed formulations. The combination is extruded into tapes or mold-pressed into panels. The properties of the combination are as follows:

Tensile Strength:	1389psi (9.58MPa)
Elongation:	200%
Extrudability:	Excellent
Moldability:	Excellent
Anti-tearing Strength:	40 lb/in (70.05N/cm)
Shore's Hardness:	84A
Limit Oxygen Index:	34%
Smoke Dust Test:	No smoke

Halogen Content: 0.0076%

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The combination similar to that in Implementation 14 is prepared. In the combination, the 52.5% ATH in the above Implementation is replaced by 50.3% ATH plus 2.2% Emtall 500 talc.

The combination has the following properties:

Tensile Strength:	1397psi (9.63MPa)
Elongation at Break:	245%
Shore's Hardness:	84A
Anti-tearing Strength:	43 lb/in (75.3N/cm)
Limit Oxygen Index:	30%
Extrudability:	Excellent
Moldability:	Excellent
Smoke Dust Test:	No smoke
Halogen Content:	0.0076%

Implementation 16

A 2.50inch diameter extruding machine and porous diaphragm threaded rod with 3:1 compression ratio are applied to extrude the combination in Implementation 4 into 360mil (9.14mm) external diameter wire. The cable sleeve thickness is 40mil and the draw ratio

is 1.93:1. The fusion temperature is 380°F(193°C).

Implementation 17

At 400°F (204°C) temperature and 30,000psi (206.8MPa) pressure, the die casting method (press forming method) is applied to press the combination in Implementations 4, 7 and 15 into 75mil (1.9mm) thick plate. The plate is used as panel in aerospace vehicles or vessels.

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Implementation 18

0.5% anti-adhesion agent is distributed on the combination prepared in Implementation 12. Such anti-adhesion agent includes Emtall 500 anti-adhesion agent produced by Engelhard, Vertal talc produced by H. M. Royal, Mistron vapor FA 750 high-density polyethylene powder produced by Cyprus Inc., and Maglite D magnesia powder produced by Calgon. These anti-adhesion agents increase the tensile strength to 1703, 1683, 1690, 1677, and 1953psi (11.74, 11.60, 11.65, 11.56, and 13.47MPa) respectively.

Implementation 19

A combination is prepared using 34.0% propylene acrylate elastomer used in Implementation 4, 16.0% polyester elastomer used in Implementation 4, and 50.0% charguard 329 fire-retardant filler.

The sum of the weight percentages is 100%. The combination is modified using 2% weight Naugaurd 445 antioxidant, 0.5% Irganox 1010, 0.5% DLTDP antioxidant promoter, 2.7% carbon black, and 0.14% VAROX vulcanizer. In the test, the combination shows excellent mechanical properties, good fire resistance, and less smoke generated in combustion.

Implementation 20

A combination is prepared in a laboratory Banbury blender. The combination contains 50% ATH used in Implementation 4, 15% polyamide elastomer (the specific weight is 1.01; the melting point is 173°C; the fusion index under 325°C and 1kg, 2mm square block is 3g/10min; the elongation is 380%), and 35% ethylene-propylene-diene terpolymer elastomer. The combination also contains 2% Nauguard 445, 0.5% Irganox 1010, 0.5% DLTDP and 0.14% VAROX vulcanizer. In the test, the combination shows excellent mechanical properties, good fire resistance, and less smoke generated in combustion.

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Implementation 21

A combination is prepared using 50% ATH used in Implementation 4, 15% polyester elastomer used in Implementation 4, and 35% another polyamide elastomer (the specific weight is 1.01; the melting point

is 148°C; the fusion index under 235°C and 1kg, 2mm square block is 9g/10min; the elongation is 715%). The combination also contains 2% Nauguard 445, 0.5% Irganox 1010, and 0.5% DLTDP. In the test, the combination shows excellent mechanical properties, good fire resistance, and less smoke generated in combustion.